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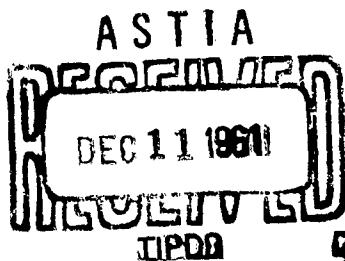
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**THE PYROLYSIS OF
O-CHLOROBENZALMALONONITRILE
IN A GAS FLOW SYSTEM**

BY

E. PORTER
D.V. SINKINSON
and
T.F.S. TEES



PORTON TECHNICAL PAPER No. 788

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THE PYROLYSIS OF O-CHLOROBENZALMALONONITRILE IN A GAS FLOW SYSTEM

by

E. PORTER, D.V. SINKINSON AND T.F.S. TEES

SUMMARY

To assist studies on the dispersion of o-chlorobenzalmalononitrile (CS) in the atmosphere from thermal generators, and as part of a general investigation of the chemical reactivity of CS, a study has been made of the pyrolysis of the compound which occurs during passage in a carrier gas stream through a heated silica tube. The effects of changes in the pyrolysis conditions, e.g. tube temperature, surface area of heated silica, nature of the carrier gas, concentration of CS, flow rate (i.e. residence time in the hot zone), on the extent and nature of the pyrolysis of CS have been examined.

Decomposition in nitrogen has been found to produce resinous substances which have not been identified; decomposition in oxygen results in the formation of simple products which have been identified and determined quantitatively. Conclusions are drawn as to the significance of the results with regard to the dissemination of CS from pyrotechnic mixtures.

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THE PYROLYSIS OF O-CHLOROBENZALMALONONITRILE IN A GAS FLOW SYSTEM

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INTRODUCTION

Solid C.W. agents may be dispersed either by mechanical or thermal means, the method of choice depending on the physical and chemical properties of the agent and the practical requirements of the situation (1). In all cases, the aim is to achieve maximum efficiency, i.e. the distribution of the maximum possible quantity of agent in its most active form. In order to obtain high efficiency by the thermal method of dispersion, the agent must possess adequate stability under the operative conditions of the generator. These conditions are, (i) the temperature, (ii) the effective contact time at the high temperature, (iii) other conditions affecting chemical reactivity, e.g. nature of molecular environment, presence of catalysts etc. To assist studies on the dispersion of o-chlorobenzalmalononitrile (CS) in the atmosphere it was necessary to obtain practical information on the thermal stability of CS under the conditions which might exist during thermal dispersion.

Of the two possible experimental methods for pyrolytic studies, i.e. the static and dynamic flow methods, the latter method seemed to be most suitable for studying the relationship between the decomposition of CS and its residence or contact times at various temperatures: this being the main information required. The results of these studies are described in this report.

EXPERIMENTAL

The apparatus is shown diagrammatically in Fig.1 and details of construction are given in the Appendix. The experimental procedure is outlined below.

The furnaces were brought to the required temperatures and the pure dry carrier gas (oxygen or nitrogen) was passed through the apparatus (not including the carburetter and CS filters) for 20 - 30 minutes to remove any traces of water. After preheating the carburetter - previously weighed

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complete with CS charge - in a gas flame, the complete apparatus was assembled and the run started by adjusting the flow rate of the carrier gas to the desired value. At the termination of the run, the carburetter was removed for reweighing and the gas flow was continued for 10-15 minutes to carry residual traces of undecomposed CS into the condenser. The apparatus was then dismantled and the pyrolysis tube was cleared of waste products by heating at 600-700°C in an air stream.

Recovery of CS from the condenser and filter units was achieved by three solvent washes: acetonitrile, alcohol, and water were used successively. The two organic solvent fractions, which had been specially purified and dried before use, were mixed, made up to a known volume, acidified with perchloric acid /a few drops (2) / and the CS content was measured by the UV absorption method (3). It was assumed that the pyrolysis products did not introduce serious errors into the estimation since the absorption spectrum corresponded to that of pure CS over the spectrum range 2400 - 3200A. Ammonium chloride, which was present in the aqueous wash (v.s.), was estimated as chloride by Volhard's titration method.

As may be seen in Table 2, various other CS decomposition products were collected and estimated. Water was collected in dry alcohol (cooled with 'cardice') and was determined by the Karl Fischer method. Hydrocyanic and hydrochloric acids were determined (in total) gravimetrically by precipitation as the silver salts and were differentiated by repeating the precipitation on a fresh solution after boiling off the hydrocyanic acid. Carbon monoxide was measured as its addition compound with palladous chloride ($PdCl_2 \cdot CO$), and also by gas analysis with a Haldane type apparatus; the latter apparatus was also used to measure carbon dioxide. Nitrous oxide and acetylene were estimated by infra red gas analysis procedures.

RESULTS

The relationship between the CS concentration and the extent of pyrolysis is shown in Table 1, and analytical results are given in Table 2 and Fig.5. Variations in the percentage recovery of CS with the tube temperature for various gas flow rates are shown graphically in Figs.2 and 3. The usual rate relationships are shown in Figs.4A and 4B, the data for these graphs having been derived from that given in the preceding figures. Flow rates and contact times at various temperatures are tabulated in Table 3.

DISCUSSION

The high thermal stability of CS shown in the present work (Ref. Figs.4A and 4B) is not surprising in view of the absence of thermally labile groups in the molecule, and also since it is known that unsaturated nitriles may be prepared in high yield by the catalytic dehydrogenation

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of the saturated compounds at temperatures of 600°C (4). The present data show that CS decomposes slowly in nitrogen at 700°C (30% decomposition in 20 sec) and somewhat more rapidly in oxygen (30% decomposition in 120 sec at 500°C). The former reaction in nitrogen results in the formation of resinous products (probably polymeric) which have not been identified; the latter reaction in oxygen results in the complete breakdown of the molecule to simpler products (Table 2 and Fig.5), an almost quantitative yield of carbon oxides being formed at the higher temperatures. It is likely that ammonia is formed by gaseous hydrolysis of the cyano groups; acetylene probably arises as a result of the rupture of the benzene ring, and nitrous oxide is probably formed as a result of reduction of the higher oxide of nitrogen by ammonia.

Both pyrolytic reactions are subject to surface effects (Figs.2B and 3B) which, in the case of the silica wool packing, may result either from an increase in heat transfer efficiency or reactions at the surface. Both reactions are independent of CS concentration (within the limits of experimental error) over the concentration range $0.02 - 0.8 \text{ g.l.}^{-1}$ (Table 1), and the reaction rates are not explicable in terms of any simple kinetic law.

The available data on the functioning of pyrotechnic munitions charged with chlorate/sucrose/CS mixtures (5) indicate that the maximum temperature attained in the mixture is about 700°C and the contact time not greater than one second; further, that the dissemination efficiency is dependent on the proportions of the constituents of the mixture and on their particle sizes. Under optimum conditions efficiencies of 98% may be achieved.

If the dispersion process is considered as consisting of two stages - (i) the heterogeneous combustion reaction during which the CS is volatilized: (ii) the ejection process during which the volatilized CS and the waste gases, formed during the combustion, are expelled from the munition (6) - then, it is probable that the temperature of 700°C is only attained during stage (i) and that the one second contact time is sufficient to complete both stages. During stage (i) the CS is volatilized whilst in contact with an oxidising agent: during stage (ii) it is expelled to the atmosphere whilst in contact with inert or reducing combustion products (providing that the oxidising agent/fuel ratio is not too high). Since dissemination efficiencies of 98% have been achieved it is clear that by regulating the combustion conditions decomposition may be almost totally eliminated. However, the present results permit the conclusion that decomposition is more likely to occur during stage (i) than during stage (ii), (Ref. Fig.4A), and this conclusion should be of assistance to those devising new CS dissemination devices.

CONCLUSIONS

1. CS has a high thermal stability in an inert gas phase but is decomposed more rapidly in an oxidising atmosphere.

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2. Pyrolytic decomposition in nitrogen results in the formation of resinous products (probably polymeric); in oxygen, conversion to simple oxidation products occurs.
3. In the dissemination of CS by pyrotechnic mixtures decomposition is only likely whilst the agent is in an oxidising environment.

ACKNOWLEDGEMENTS

Assistance in the identification and estimation of pyrolysis products by infra-red methods was given by L.C. Thomas. Useful discussions on the methods of dispersing CS were held with M.A.P. Hogg.

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Details of the Pyrolysis apparatus (Fig.5)

- CS Carburetter:- Charge 3 g: renewed for each run in oxygen. Enclosed in an electrically heated aluminium jacket controlled at a definite temperature within the range $130-160^{\circ}\text{C}$.
- Pyrolysis tube: A transparent vitreosil tube. Length 97 cm: internal diameter 2.5 cm: internal surface area 760^2cm^2 : internal volume 475 ml. Packed with silica wool:- 10 g of 5-20 μ diameter fibres of surface area 4350 - 17,400 cm^2 . Lined with asbestos tape:- 194 cm length of 3 cm tape. Apparent temperature variation $\neq \pm 5^{\circ}\text{C}$ along length (excluding a 10 cm jointed length at both ends).
- Furnace heater:- A glazed vitreosil tube wound with 19 gauge Kanthal wire, total resistance 28 ohms (cold). Covered with alundum and kaolin silicate cements and lagged with asbestos cloth.
- Thermocouples:- Chromel alumel thermocouples used in pyrolysis tube. Calibrated in sulphur vapour (444.6°C) and in freezing aluminium (658.9°C). Connected directly to a Cambridge Spot Galvanometer.
- Filter:- 18.5 cm diameter discs of glass fibre paper (Whatman GF/B) backed by a hardened cellulose filter paper (Whatman No.42) and held in an anti-leak jig.

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TABLE 1THE RELATIONSHIP BETWEEN CS CONCENTRATION AND % RECOVERY

- (a) Oxygen as carrier gas.
- (b) Nitrogen as carrier gas.

CS Conc. g.l.	Flow rate l.h ⁻¹	Furnace Temp. °C	% Recovery
(a) 0.031	15	590	9
(a) 0.049	15	590	11
(a) 0.106	15	590	7.5
(a) 0.036	5	553	25.5
(a) 0.091	5	553	21
(b) 0.016	30	750	35.8
(b) 0.027	30	750	40.6
(b) 0.076	30	750	36.0
(b) 0.072	30	750	32.5

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TABLE 2PRODUCTS IDENTIFIED AFTER THE PYROLYTIC DECOMPOSITION OF CS IN OXYGEN

Furnace Temp. °C	Moles of products per mole of CS								
	CS	CO	CO ₂	H ₂ O	Cl ⁻	CN ⁻	NH ₃ ⁺	N ₂ O	C ₂ H ₂
625	0.05	9.0	1.2	2.1	1.0	-	0.34	0.32	Trace
615	0.18	5.2	-	-	-	0.18	-	0.22	0.09
595	0.42	2.4	-	-	0.32	0.6	-	-	
587	0.52	2.0	-	-	-	-	-	-	
563	0.82	0.74	-	-	-	-	-	-	
530	1.0	0.03	-	-	-	-	-	-	
490	1.0	Nil	-	-	-	-	-	-	

1 Mole CS = 10M CO; 10M CO₂; 2.5M H₂O; 1M N₂O; 2M NH₃; 3(4)M C₂H₂;
 1M Cl⁻; 2M CN⁻.

CS concentration = 0.02 g.l.⁻¹.

Oxygen flow rate = 50 l.h⁻¹.

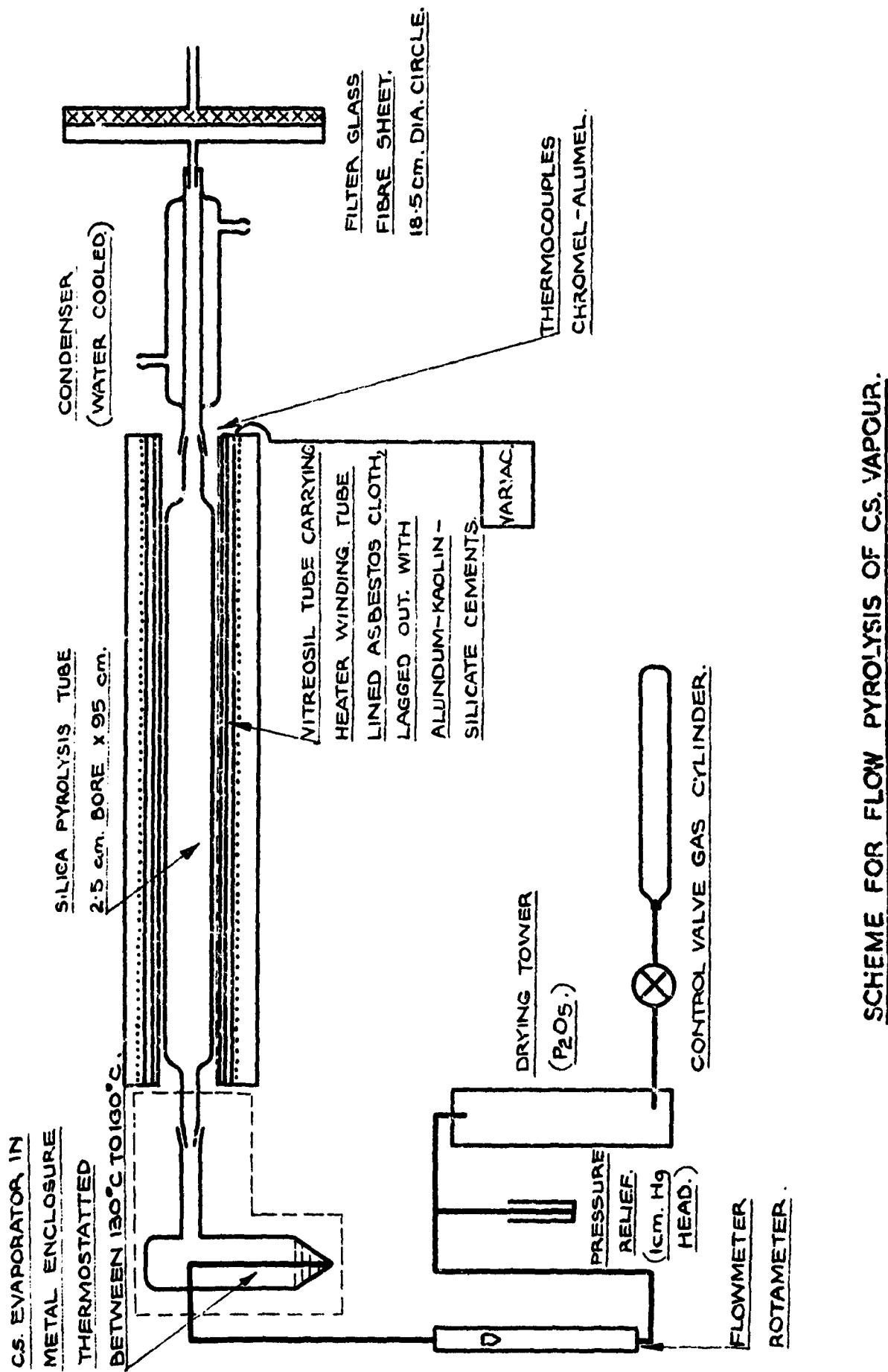
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TABLE 3
CONTACT TIMES (SEC)

Flow rate l.h ⁻¹	5	10	15	30	50	100
Temperature °C						
400	138.0	69.0	46.0	23.0	13.8	5.8
500	120.6	10.3	40.2	20.1	12.1	5.0
550	113.4	56.7	37.8	18.9	11.3	4.7
575	110.0	55.0	36.6	18.3	11.0	4.6
600	106.8	53.4	35.6	17.8	10.7	4.5
700	95.8	47.9	31.9	15.9	9.6	4.0
750	91.4	45.7	30.5	15.2	9.1	3.8
800	87.0	43.5	29.0	14.5	8.7	3.6

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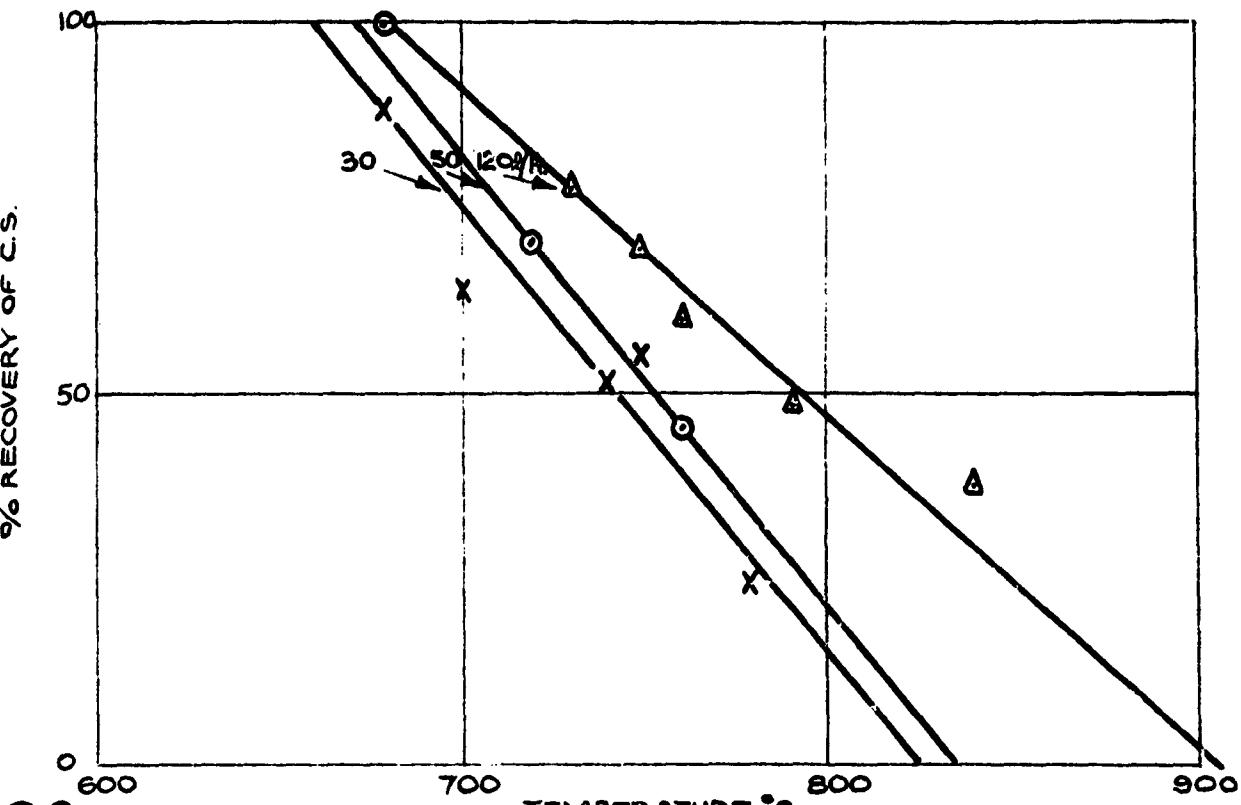
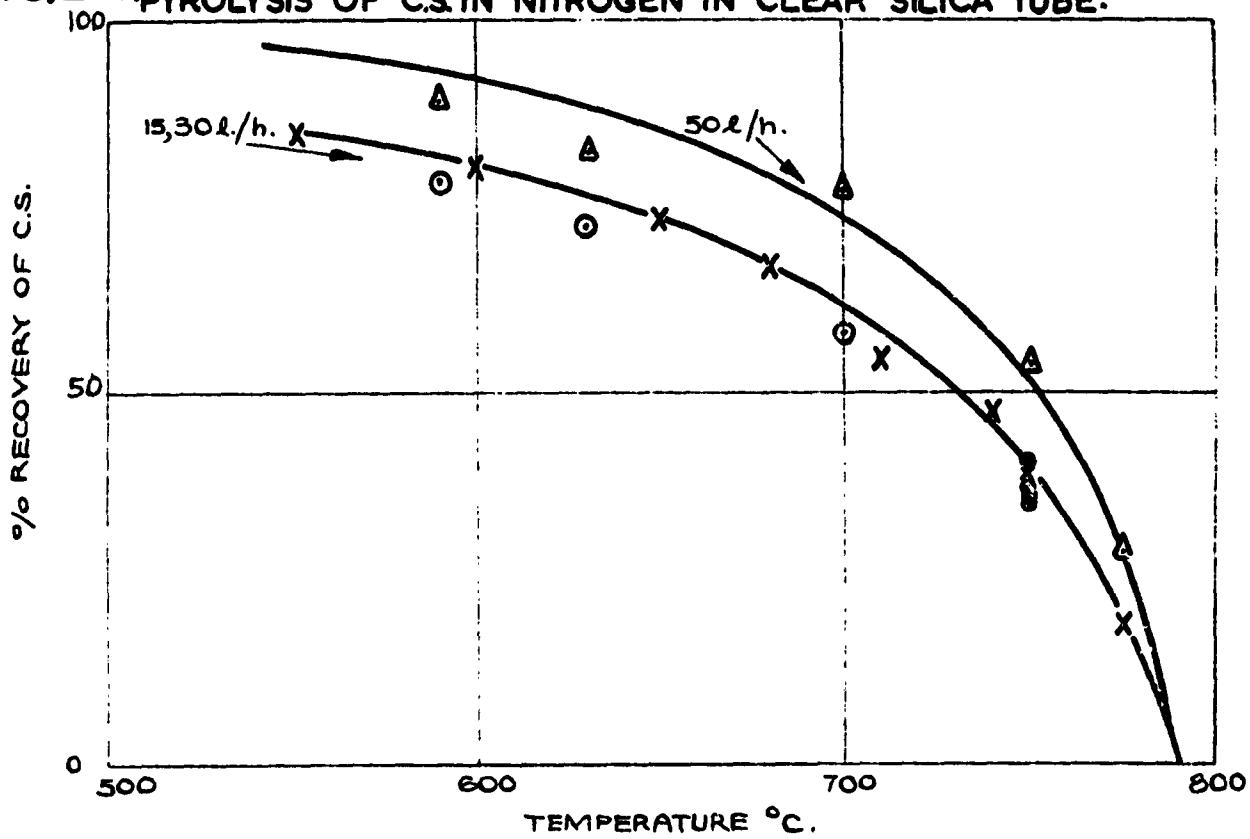


FIG. 2 a. PYROLYSIS OF C.S. IN NITROGEN IN CLEAR SILICA TUBE.



PYROLYSIS OF C.S. IN NITROGEN IN PACKED SILICA TUBE.

FIG. 2 b.

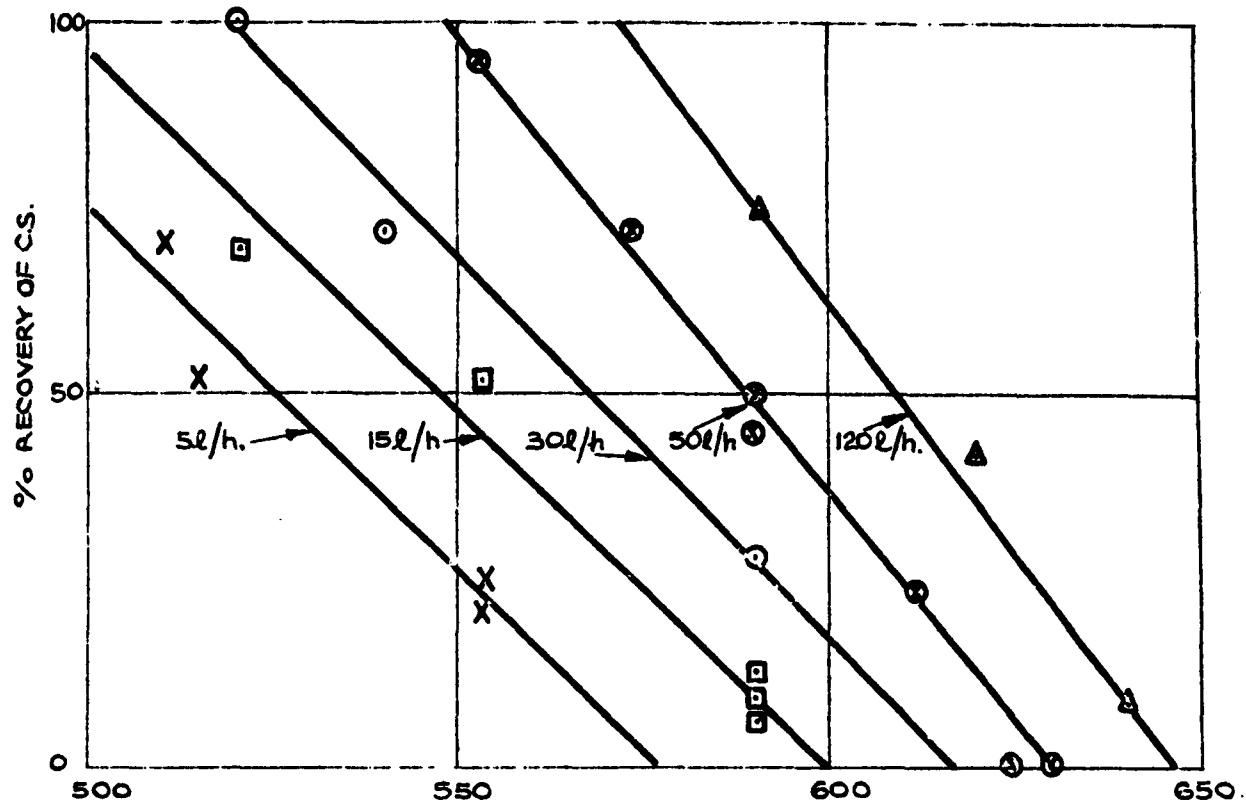
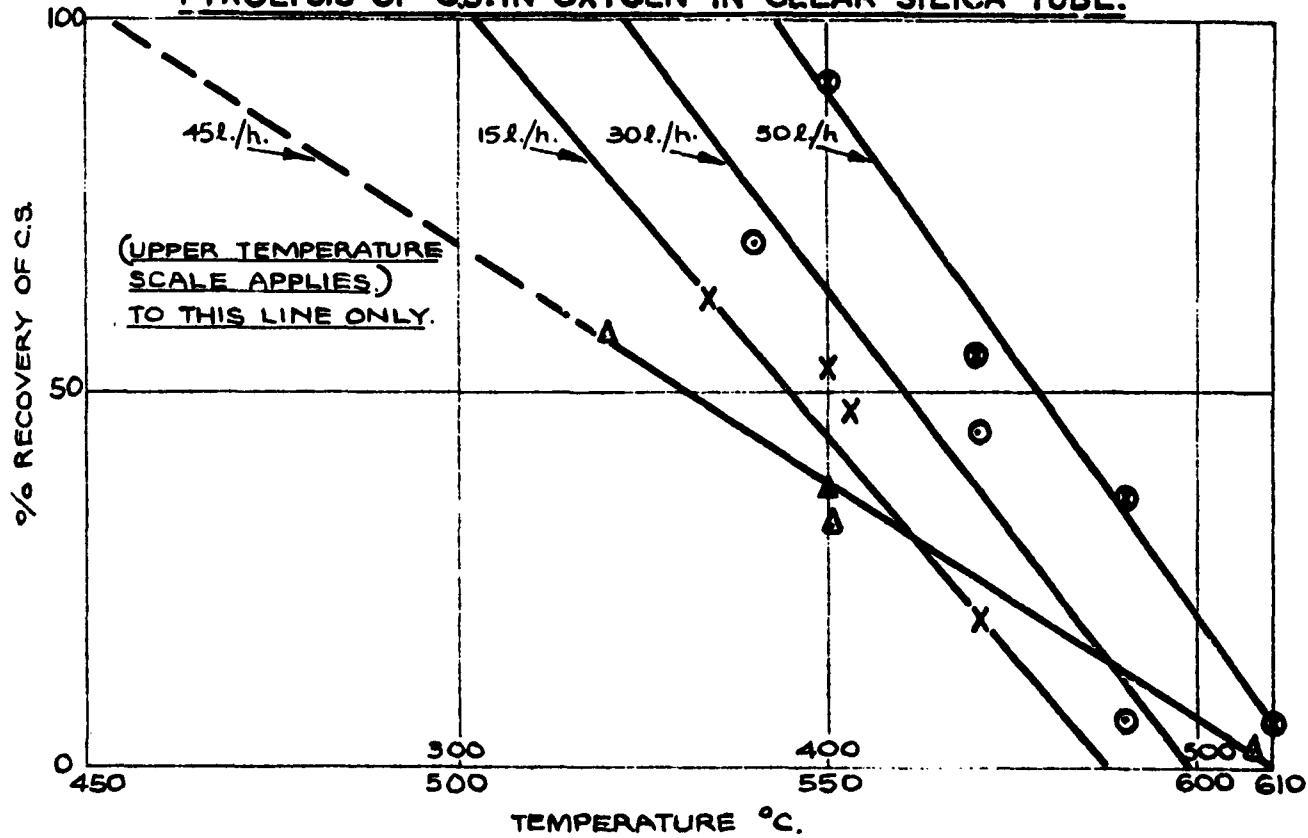


FIG. 3a. PYROLYSIS OF CS. IN OXYGEN IN CLEAR SILICA TUBE.



PYROLYSIS OF CS. IN OXYGEN IN PACKED SILICA TUBE.

FIG. 3b.

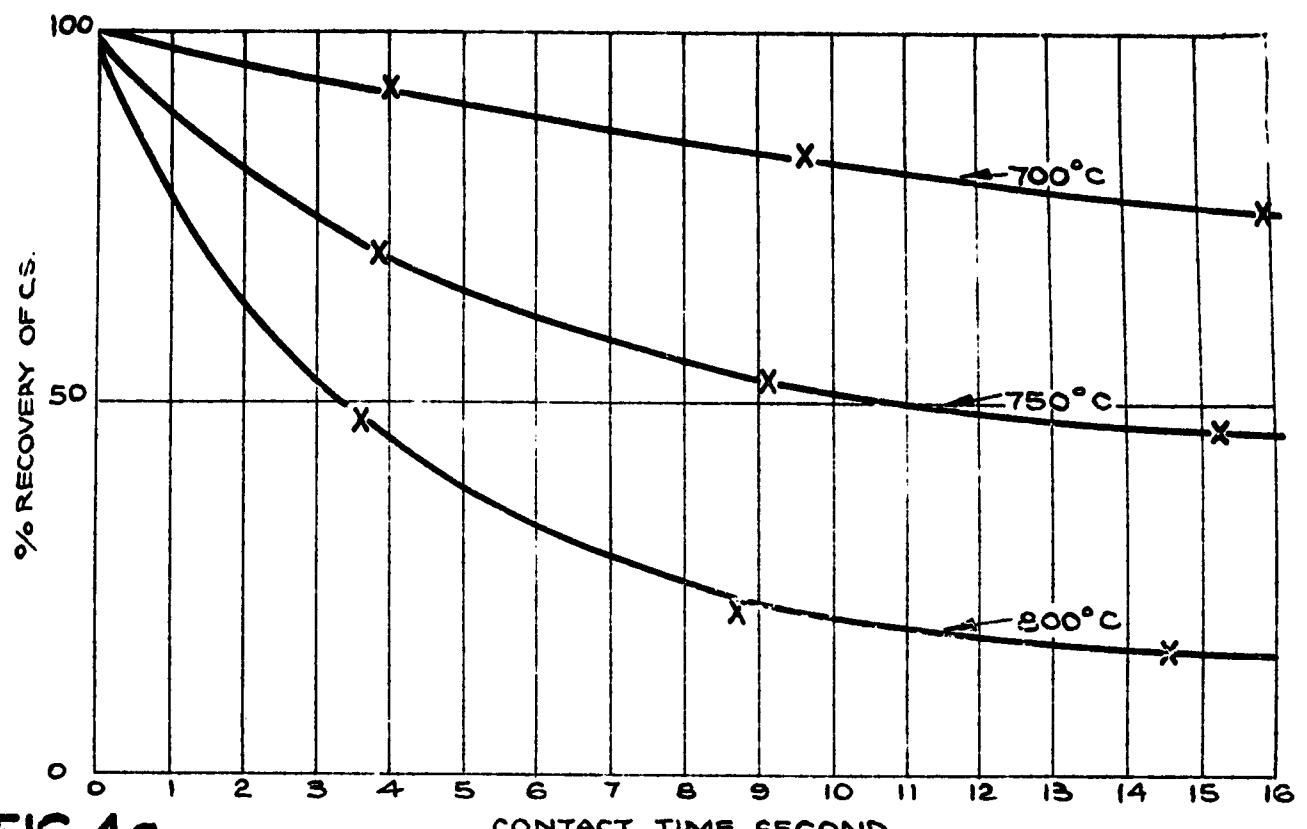
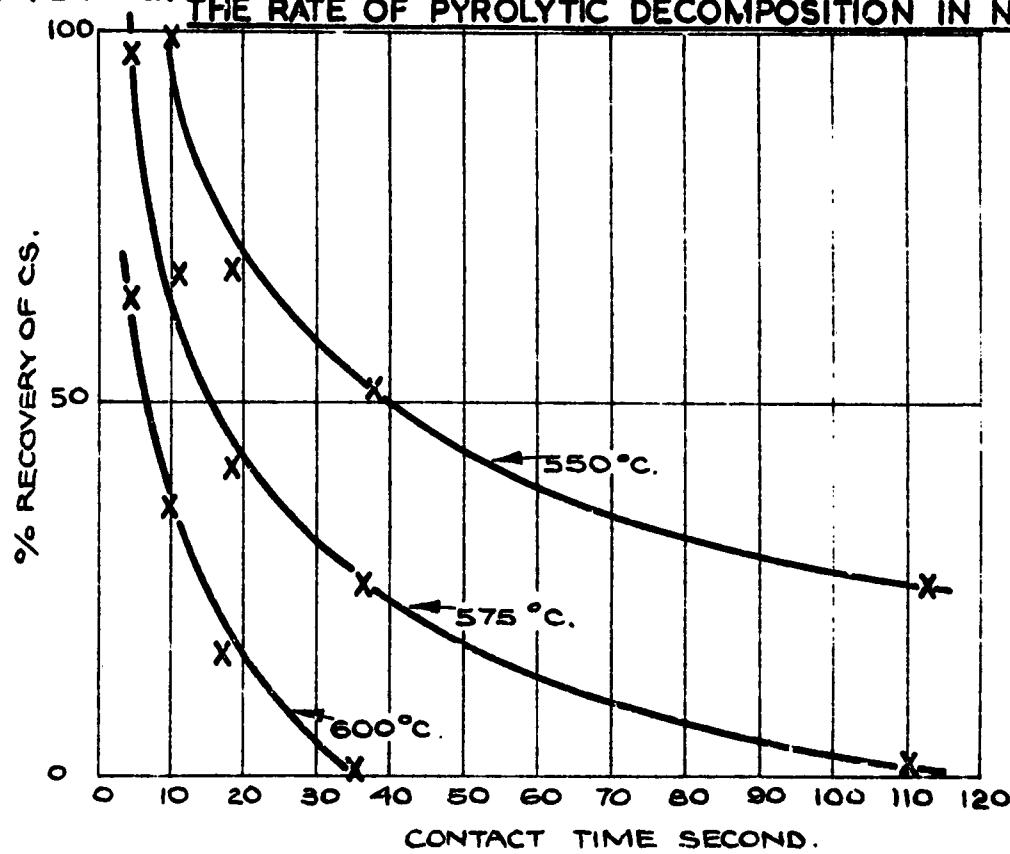
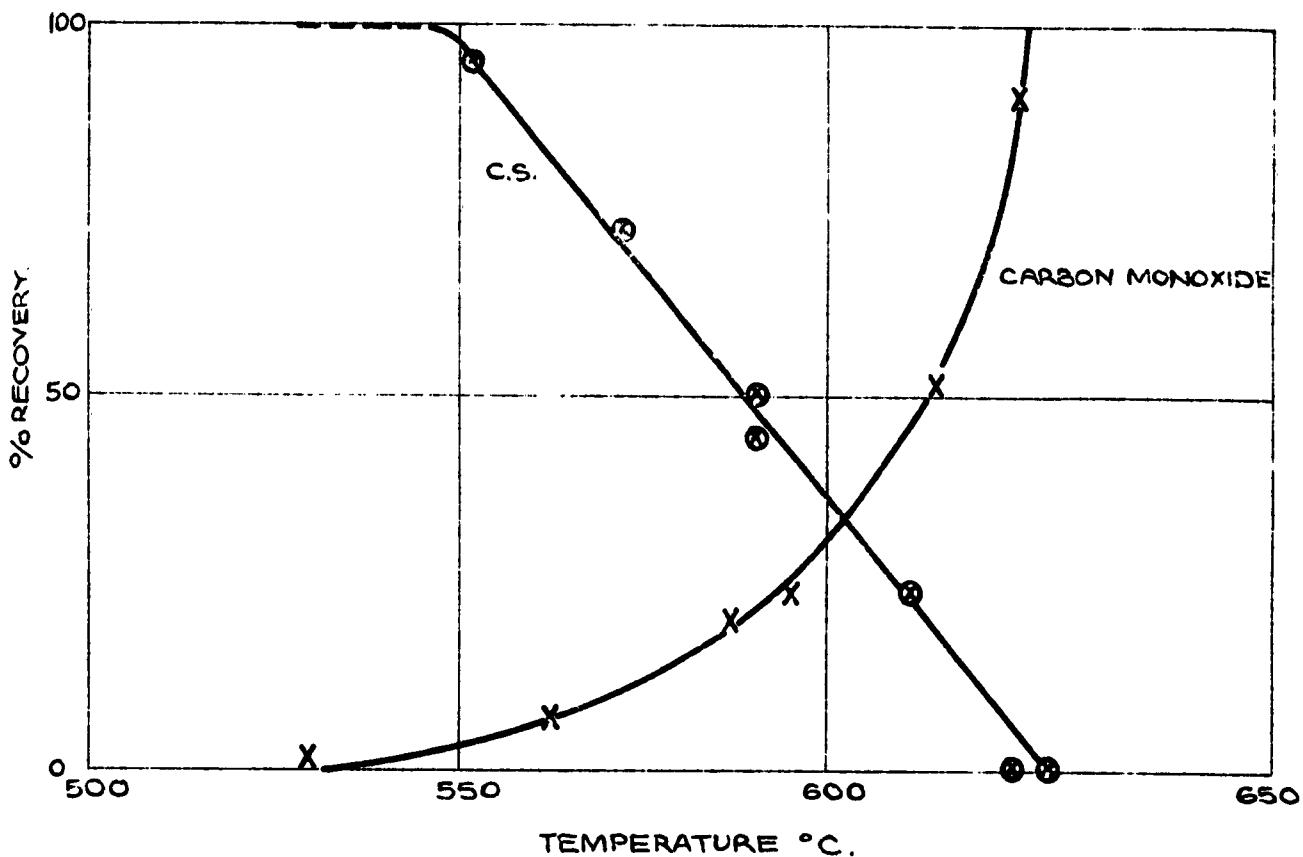


FIG. 4a. THE RATE OF PYROLYTIC DECOMPOSITION IN NITROGEN.



THE RATE OF PYROLYTIC DECOMPOSITION IN OXYGEN.

FIG. 4 b.



THE FORMATION OF CARBON MONOXIDE FROM GS. DURING PYROLYSIS
IN OXYGEN. (FLOW RATE 50 l/h.)

FIG. 5.

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